Acknowledgment.—The authors wish to thank Mr. E. M. Hadsell and Miss J. N. Whiteman for the fractional distillations reported herein. The authors are also grateful to Dr. E. W. Balis and Mrs. Miriam Lennig for the carbon and hydrogen determinations, and to Mr. L. B. Bronk and Mrs. Grace Poellmitz for molecular weight and density determinations.

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Dimethylvinylethoxysilane and Methylvinyldiethoxysilane

BY M. COHEN AND J. R. LADD

RECEIVED NOVEMBER 12, 1952

A mixture of magnesium (2.63 moles) and absolute ether (800 ml.) was placed in a two-liter, three-necked, round-bottom flask equipped with a mercury-sealed stirrer, Dry Ice condenser and a gas inlet tube. A stopcock had been previously sealed to the bottom of the reaction flask. Methyl bromide was bubbled into the stirred mixture until all the magnesium had dissolved.

After excess methyl bromide had been allowed to evaporate from the solution, the methylmagnesium bromide solution was added to a stirred solution of 500 g. (2.63 moles) of vinyltriethoxysilane[1] and 960 ml. of ether in a three-liter, three-necked, round-bottom flask equipped with a mercury-sealed stirrer and a water condenser. All outlets were protected with calcium chloride tubes. The rate of addition was such that the ether refluxed gently.

The mixture was stirred under reflux one hour, and the ether distilled off. The distillation was continued at atmospheric pressure until the temperature of the distillate reached 100°. The remainder of the silanes was separated from the residue of magnesium salts at reduced pressure (40 mm.). On fractionation of the combined silanes there was obtained 19 g. (5.6% yield) of vinyldimethylethoxysilane, b.p. 99°, $n^{20}D$ 1.3983, d^{20}_4 0.790; *MR* calcd.[2] 39.8, obsd. 39.8; and 241 g. (57.4% yield) of vinylmethyldiethoxysilane, b.p. 133 to 134°, $n^{20}D$ 1.4000, d^{20}_4 0.858; *MR* calcd.[2] 45.2, obsd. 45.3.

Anal. Calcd. for $C_6H_{14}OSi$: C, 55.3; H, 10.8; Si, 21.5. Found: C, 55.4; H, 11.1; Si, 21.0. Calcd. for $C_7H_{16}O_2Si$: C, 52.5; H, 10.1; Si, 17.5. Found: C, 52.5; H, 10.2; Si, 17.2.

(1) Linde Air Products, New York, N. Y.

(2) E. L. Warrick, THIS JOURNAL, **68**, 2455 (1946).

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Thiosemicarbazones of Thiophene Derivatives[1]

BY E. CAMPAIGNE, P. A. MONROE, B. ARNWINE AND W. L. ARCHER

RECEIVED JULY 31, 1952

Due to the effectiveness of *p*-acetaminobenzaldehyde thiosemicarbazone (Tibione)[2] as an antituberculous agent, a number of thiosemicarbazones have been prepared for biological testing. Among these have been a number of heterocyclic derivatives, including several of the thiophene series. 2-Thenaldehyde thiosemicarbazone has been reported to have a relatively high order of activity against the tubercle bacillus *in vitro*.[3,4] In addition, Anderson, *et al.*,[4] reported *in vitro* tests on the thiosemicarbazones of 2-acetothienone, 2-propiothienone, 2-butyrothienone and 2,5-dimethyl-3-acetothienone. Of these, 2-propiothienone thiosemicarbazone afforded the best protection. A later report[5] indicated that 2-thenaldehyde thiosemicarbazone gave weak protection to mice infected with tuberculosis.

In recent papers[6,7] Hamre, *et al.*, reported that *p*-aminobenzaldehyde thiosemicarbazone caused a significant delay in death of chick embryos and mice infected with vaccinia virus. This observation was confirmed by Thompson, Price and Minton[8] who reported that benzaldehyde thiosemicarbazone prevents multiplication of vaccinia virus in check embryonic tissue, but that substitution in the *p*-position of the benzene nucleus reduced virostatic activity.

In pursuing a program of virus chemotherapy, we have synthesized a number of heterocyclic thiosemicarbazones, and report here a group of thiophene derivatives. All of the carbonyl compounds used in preparing the thiosemicarbazones have been reported previously, either from these laboratories, or from other sources. The compounds prepared, their melting points and analyses are presented in the table. The biological testing data have been reported elsewhere by Dr. R. L. Thompson.[9]

TABLE I

THIOSEMICARBAZONES OF THIOPHENE DERIVATIVES

Cmpd. No.		M.p., °C.[a]	Formula	Nitrogen, % Calcd.	Found
	3-Thenaldehydes				
1	Unsubstituted	151–152	$C_6H_7N_3S_2$	22.78	22.70
2	2-Chloro-	196–198 dec.	$C_6H_6N_3S_2Cl$	19.15	19.06
3	2-Bromo-	192–194 dec.	$C_6H_6N_3S_2Br$	15.91	15.64
4	2,5-Dichloro-	232–233 dec.	$C_6H_5N_3S_2Cl_2$	...[b]	...[b]
	2-Thenaldehydes				
5	5-Chloro-	164–165	$C_6H_6N_3S_2Cl$[c]	19.15	19.27
6	5-Bromo-	182–184	$C_6H_6N_3S_2Br$	15.91	15.97
7	5-Nitro-	252–255 dec.	$C_6H_6N_4O_2S_2$	24.36	24.05[d]
8	5-Acetamido-	231–233	$C_8H_{10}N_4OS_2$	23.15	23.05[d]
9	5-Methyl-	160–161	$C_7H_9N_3S_2$	21.08	21.02[d]
10	3-Methyl-	185–187	$C_7H_9N_3S_2$	21.08	21.40[d]
11	5-*t*-Butyl-	182–183	$C_{10}H_{15}N_3S_2$	17.42	17.40
	2-Acetothienones				
12	Unsubstituted[e]	147–148	$C_7H_9N_3S_2$	21.08	21.12[d]
13	5-Bromo-	200–201	$C_7H_8N_3S_2Br$	15.11	14.99[d]
14	5-Methyl-	161–163	$C_8H_{11}N_3S_2$	19.73	19.72[d]
15	4-Nitro-5-methyl-	232–235 dec.	$C_8H_{10}N_4O_2S_2$	21.72	21.48[d]

[a] All melting points uncorrected. [b] Calcd.: S, 25.2; Cl, 28.0. Found: S, 25.2; Cl, 27.9. [c] Calcd.: S, 29.16. Found: 29.06. [d] Analyses by H. L. Clark, Urbana, Ill. [e] Previously reported by F. E. Anderson, C. J. Duca and J. V. Scudi, THIS JOURNAL, **73**, 4967 (1951), m.p. 148–149° uncor.

(1) Contribution No. 571 from the Chemistry Laboratory of Indiana University. This work was supported by a contract between the Office of Naval Research, Department of the Navy, and Indiana University.

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